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IV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

THERMOELECTRIC LINE OF COPPER AND NICKEL BELOW 0°.

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THE great difficulty to be encountered in experiments on thermo-electricity is the variation in the results obtained by different experimenters. There can be no comparison with previous experiments when all the results are different. As an example, take the electromotive force of a junction of bismuth and copper — with one junction at 0° and the other at 100° — as obtained by different experimenters: —

Wheatstone	0.00106
Neumann	0.00390
J. Regnault	0.00286
E. Becquerel	0.00483

These results are referred to the electromotive force of a Daniell element as unity.

It will be observed that the last result is over four times as great as the first.

There are many causes which might produce this variation. Slight differences in the structure of the metals often affect the results, and the results obtained with the same metal, before and after it has been subjected to pressure and tension, are often very different. A piece of hard steel always gives different effects from a piece of soft steel. But these causes must all be of minor importance; the great trouble consists in the impurity of the metals. It is well known that other electrical properties of metals are greatly changed by slight differences in purity. Thus the specific resistance of copper may be increased fifty per cent by the presence of slight impurities.

It is, therefore, of the greatest importance to use absolutely pure substances in all experiments on thermoelectricity. In the following experiments, therefore, the metals used have always been chemically pure, — deposited by electrolysis.

The first experiments were made with copper and nickel. The nickel was about twelve inches long and V-shaped. To each end was soldered a strip of copper, about eight inches long. During the experiment one end was placed in melting snow and the other in a mixture of snow and calcic chloride, — 30 grammes of snow to 40 of calcic chloride. The two junctions, and also the metals as far as they were in contact with the freezing mixture, were coated with shellac. A mercury thermometer — the zero point of which had previously been verified — was bound to the colder junction of the copper and nickel. Copper wires, soldered to the free ends of the two strips of electrolytic copper, connected the thermoelectric element with the galvanometer, the circuit being made or broken by means of a key. The galvanometer was a Thomson's mirror galvanometer of low resistance. The mixture of snow and $CaCl_2$ generally gave a temperature of about — 25° C. From this the temperature gradually rose, and at every 5° increase the circuit was made, and the deflection of the galvanometer observed. When the temperature had reached 0° the junction was placed in a vessel of water and heated gradually to about 80°C, the deflection of the galvanometer being observed for every ten degrees increase of temperature. The following are the results from five series of experiments. The junctions were reversed in every alternate series; that is, the junction that, in the first, was placed in melting snow, was, in the second, placed in $CaCl_2$ and snow. This obviated whatever irregularities might arise from any difference between the two junctions.

The first column gives the temperature of the colder junction. The second the number of the experiment. The third the resistance of the whole circuit and the galvanometer. The resistance of the latter was six ohms. The fourth gives the deflection of the galvanometer needle. The fifth gives the product of this deflection into the resistance, which is directly proportional to the electromotive force.

t	Number of Experiment.	Resistance. R	Deflection. d	$d \times R$
—25°	2	36	14.5	522.0
"	4	36	15.0	540.0

Mean value of $d \times R = 531.0$.

Temperature. t	Number of Experiment.	Resistance. R	Deflection. d	$d \times R$	Mean value of $d \times R$.
—20°	1	56	8.4	470.4	
"	2	36	11.5	414.0	
"	5	36	12.6	453.6	446.0
—15°	1	56	6.1	341.6	
"	2	36	8.3	298.8	
"	3	36	7.7	277.2	
"	4	36	9.8	352.8	
"	5	36	8.8	316.8	315.4
—10°	1	56	4.2	235.2	
"	2	36	4.8	172.8	
"	3	36	5.2	187.2	
"	4	36	6.0	216.0	
"	5	36	6.5	234.0	209.0
—5°	1	56	2.1	117.6	
"	3	36	2.6	83.6	
"	4	36	2.5	80.0	
"	5	36	4.3	154.8	109.0
+10°	1	56	4.5	252.0	
"	2	36	7.5	270.0	
"	3	36	6.6	237.6	
"	4	36	6.8	244.8	
"	5	36	6.3	226.8	246.2
+20°	1	56	9.1	509.6	
"	2	36	13.5	486.0	
"	3	36	13.5	486.0	
"	4	36	14.0	504.0	
"	5	36	14.0	504.0	497.9
+30°	1	56	14.0	784.0	
"	2	86	8.6	739.6	
"	3	36	21.4	770.4	
"	4	56	14.0	784.0	
"	5	56	13.6	761.6	767.9
+40°	1	56	18.5	1036.0	
"	2	86	11.7	1006.2	
"	3	106	9.6	1020.3	
"	4	106	9.7	1028.2	
"	5	56	18.5	1036.0	1025.3
+50°	1	56	23.5	1316.0	
"	2	106	12.3	1303.8	
"	3	206	6.3	1297.8	
"	4	206	6.3	1297.8	
"	5	206	6.3	1297.8	1302.6
+60°	1	56	28.0	1568.0	
"	2	206	7.7	1686.2	
"	3	206	7.6	1565.6	
"	4	206	7.6	1565.6	1596.3

The preceding values of $d \times R$ are directly proportional to the values of the electromotive forces. The formula for the electromotive force is $E = kRd$, in which k is the constant of the galvanometer, R is the resistance of the circuit, and d is the tangent of the deflection of the galvanometer needle.

The constant of the galvanometer was determined by means of a small gas battery. The electromotive force of the gas battery was found, by means of Thomson's electrometer, to be .285 of a Daniell element. The electromotive force of a Daniell element $= 1.079$ volts, hence that of the gas battery $= 1.079 \times .285 = .307515$ volts $= 30751500$ absolute units, since one volt $= 10^8$ absolute units, in the C. S. G. system. The formula for the constant is

$$k = \frac{E'}{R'd'}$$

where $E' =$ the electromotive force of the battery, R' the whole resistance of the circuit, and d the tangent of the deflection of the galvanometer needle,

$$\therefore k = \frac{E'}{R'd'}$$

Consequently the preceding formula for the electromotive force $E = k\ R \tan \alpha$ becomes

$$E = \frac{E'}{R'd'}\ d \times R.$$

The constant by which the preceding results in the tables are to be multiplied in order to reduce the electromotive force to absolute units is then $\frac{E'}{R'd'} = k$.

It was found that when $R' = 12000$ $d' = 45.0$.
" " " $R' = 11000$ $d' = 50.5$.

The first gives for $k = 56.9$; the second 55.3; mean value of $k = 56.1$.

Hence to obtain the absolute values of the electromotive forces the values of $d \times R$ given by the tables must be multiplied by 56.1.

After the preceding experiments a still lower temperature was obtained by means of solid carbonic dioxide and ether. Two experiments were made, the temperatures in the first being measured by an ether thermometer, in the second by an air thermometer. In both the same metals, copper and nickel, employed in the previous experiment, were used.

In the first experiment the cold mixture was placed under the receiver of an air pump. The exhaustion was maintained by means of a Richard's air pump. This occasioned a faster evaporation of the ether, and a consequent greater decrease of temperature, than could otherwise have been maintained.

The results obtained are as follows: —

Temperature given by Ether Thermometer.	Resistance. R	Deflection. d	$d \times R$
—40°	96	16.2	1555.2
—52.5°	96	20.0	1920.0
—52.5°	96	19.5	1872.0
—52.0°	96	18.7	1715.2

In the second experiment the temperatures were measured by means of the air thermometer. The bulb of the air thermometer, the junction of copper and nickel, and the bulb of the ether thermometer, were placed side by side and surrounded with solid carbonic dioxide, over which ether was poured. The simultaneous readings of the galvanometer, of the air thermometer, and of the ether thermometer were then taken, after the air thermometer had reached its lowest temperature.

The following are the results: —

Temperature given by Air Thermometer.	Temperature given by Ether Thermometer.	Resistance. R	Deflection. d	$d \times R$	Mean value of $d \times R$
60.2 C	42.3° C	106	13.5	1431.0	
"	"	206	6.8	1400.8	
"	"	156	9.0	1404.0	1411.9

In the preceding two experiments the constant of the galvanometer was obtained, as before, by means of the gas battery.

In the first experiment, $R = 14000$ $d = 47$

$$\therefore k = \frac{30751500}{14000 \times 47} = 46.7$$

In the second experiment, $R = 12000$ $d = 48$

$$\therefore k = \frac{30751500}{12000 \times 48} = 53.3$$

Consequently to obtain the values of the electromotive force for the preceding experiments the values of $d \times R$ must in the first experiment be multiplied by 46.7, in the second by 53.3.

From the preceding table it is seen that the ether thermometer cannot be used to measure temperatures accurately. The coefficient of expansion of ether is by no means constant, and besides the ether adheres to the sides of the thermometer tube. The real value of the coefficient cannot be obtained from these results, as only the bulb of the thermometer was subjected to the low temperature; but as the bulb was very large in proportion to the bore of the tube, an approximate value may be obtained.

When the temperature, as given by the air thermometer, was — 60° .2 C the ether thermometer stood at — 42° .3 C; the reading of the ether thermometer was $\frac{42.3}{60.2}$ of what it should have been if it contracted regularly. Thus temperatures in the neighborhood of — 42° C, as given by the ether thermometer, can be corrected, and more approximate results obtained, by multiplying by $\frac{60.2}{42.3} = 1.42$.

It should be remembered that the temperatures thus obtained are by no means accurate; they are only rough approximations.

Applying this correction to the temperatures given by the ether thermometer, we have: —

Temperatures given by Ether Thermometer reduced by multiplying by 1.42.	Resistance. R	Deflection. d	$d \times R$
—56.8° C	96	16.2	1555.2
—74.5° "	96	20.0	1920.0
—74.5° "	96	19.5	1872.0
—73.8° "	96	18.7	1715.2

If now the values of $d \times R$ from all the preceding tables are multiplied by the constants necessary to obtain the absolute values of the electromotive forces, the preceding results may be summed up in the following table. The first column gives the temperatures of one junction of the copper and nickel; the other junction was always at 0°. The second column gives the absolute values of the corresponding electromotive forces, in the C. G. S. system of units. The third column gives the differences between the alternate electromotive forces. And the fourth the differences between the corresponding temperatures.

Temperature.	Absolute value of the Electromotive force.	Differences between alternate Electromotive Forces.	Difference between alternate Temperatures.
+60° C	89552.43	....	...
+50° "	73075.86	16476.57	10°
+40° "	57519.33	15556.53	10°
+30° "	43079.19	14440.14	10°
+20° "	27932.19	15147.00	10°
+10° "	13811.8	14120.39	10°
— 5° "	6114.9	....	...
—10° "	11724.9	5610.0	5°
—15° "	17693.9	5969.0	5°
—20° "	25020.6	7326.7	5°
—25° "	29789.1	4768.5	5°
—56.8° "	72627.84	42838.74	31.8
—60.2° "	75254.27	2626.43	3.4
—73.8° "	80099.84	4844.57	13 6
—74 5° "	88496.5	8396.66	0.7

NOTE. — Between 74.5° and 25° the temperature rose too rapidly to obtain intermediate readings with the air thermometer.

If these results are represented by a curve, of which the abscissas are proportional to the temperatures, and the ordinates to the corresponding electromotive forces, it is seen that the curve is approximately a right line for all the points except those corresponding to the temperatures obtained by the ether thermometer. It was to be expected that these points would not lie exactly on the curve, as the temperatures were so roughly obtained.

The thermoelectric line for temperatures below 0° is almost a direct continuation of the line above 0°; the two, however, are inclined at a slight angle. The reason of this is probably due to the fact that for temperatures above 0° the piece of electrolytic copper soldered to the hot end of the nickel became more heated throughout than the piece soldered to the cold junction; and consequently the points of contact where the copper galvanometer wires joined the two pieces of electrolytic copper were unequally heated, and a subsidiary current was produced. It was found that when both junctions of copper and nickel were kept at the same constant temperature, a very small current was produced when one piece of the electrolytic copper was slightly heated above the other.

From these experiments it appears that an ether thermometer cannot be used to measure low temperatures accurately, not only because the ether adheres to the sides of the tube, but because its coefficient of expansion is variable; also that the thermoelectric line of copper and

nickel, when chemically pure, is practically straight, at least between $+ 60°$ C and $- 60°$ C.

A thermoelectric element of pure copper and nickel can therefore be used as an accurate means of measuring low temperatures.

Examination of Ether Thermometer.

After the preceding experiments the ether thermometer was more critically examined. The bulb was placed in a mixture of calcic chloride and snow, beside the bulb of a mercury thermometer; and afterwards in water, which was heated to about $+ 30°$ C.

The results are contained in the following table. The first column gives the temperatures shown by the mercury thermometer; the second column the corresponding temperatures shown by the ether thermometer.

Temperatures given by Mercury Thermometer.	Temperatures given by Ether Thermometer.	Temperatures given by Mercury Thermometer.	Temperatures given by Ether Thermometer.
+30° C	+28.0° C	—15° C	— 9.8° C
+25° "	+23.6° "	—20° "	—14.0° "
+20° "	+19.0° "	—23° "	—16.1° "
+15° "	+14.7° "	—24° "	—16.7° "
+10° "	+10.3° "	—25° "	—17.4° "
+ 5° "	+ 6.2° "	—26° "	—18.1° "
— 5° "	— 1.6° "	—60.2° "	—42.3° "
—10° "	— 5.6° "		

The zero point of the ether thermometer was determined by burying the bulb in melting snow for twenty minutes. It was then found that the true zero was 2° above the zero of the scale. Applying this correction to the preceding results, it is still seen that the ether expanded and contracted very irregularly.

It is true that only the bulb of the thermometer was subjected to the different temperatures; but the bulb was very large in proportion to the base of the tube, and as an ether thermometer must necessarily be made rather long, it is, in the great majority of cases, impossible to subject any more than the bulb to the temperature to be determined.